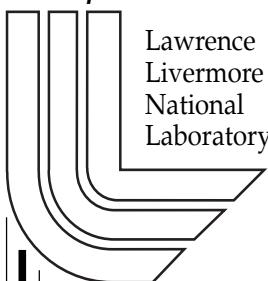


# **Calculated Thermodynamic Functions for Gas Phase Uranium, Neptunium, Plutonium, and Americium Oxides ( $\text{AnO}_3$ ), Oxyhydroxides ( $\text{AnO}_2(\text{OH})_2$ ), Oxychlorides ( $\text{AnO}_2\text{Cl}_2$ ), and Oxyfluorides ( $\text{AnO}_2\text{F}_2$ )**

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**Calculated Thermodynamic Functions for Gas Phase Uranium, Neptunium, Plutonium, and Americium Oxides ( $AnO_3$ ), Oxyhydroxides ( $AnO_2(OH)_2$ ), Oxychlorides ( $AnO_2Cl_2$ ), and Oxyfluorides ( $AnO_2F_2$ )<sup>\*</sup>**

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Based on known and estimated molecular constants, the thermodynamic functions,  $C_p$ ,  $S^\circ$ ,  $H^\circ - H^\circ(298)$ , and  $-(G^\circ - H^\circ(298))/T$ , have been calculated and tabulated for actinide vapors species of the formulas  $AnO_3(g)$ ,  $AnO_2(OH)_2(g)$ ,  $AnO_2Cl_2(g)$ , and  $AnO_2F_2(g)$  where  $An = U, Np, Pu$ , and  $Am$ . A method to calculate the thermodynamic functions for the mixed species,  $AnO_2ClOH(g)$ ,  $AnO_2FOH(g)$ , and  $AnO_2FCI(g)$ , is also given.

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## Nomenclature

$a(An,M)$	Unit cell length which varies as a function of metal cation and actinide ion
An	Actinide (U, Np, Pu, Am)
$c(An,M)$	Unit cell length which varies as a function of metal cation and actinide ion
$C(M)$	A constant which varies with metal cation
$C_p(T)$	Heat capacity
$d(An^{+n}-Cl)$	Interatomic bond length of actinide +n chlorine bond
$d(An^{+n}-F)$	Interatomic bond length of actinide +n fluoride bond
$d(An^{+n}=O)$	Interatomic bond length of actinide +n oxygen double bond
$d(An^{+n}-OH)$	Interatomic bond length of actinide +n hydroxide bond
$d(An^{+n}-X)$	Interatomic bond length of actinide +n halide bond
E	Energy of the electronic state
g	Degeneracy of the electronic ground state
$-(G^\circ(T)-H^\circ(298))/T$	Free energy function
$H^\circ(298)-H^\circ(0)$	Enthalpy at 298 K minus enthalpy at 0 K
$H^\circ(T)-H^\circ(298)$	Enthalpy at T minus enthalpy at 298 K
$K_{eq}$	Equilibrium constant
M	Metal cation (K, Rb, Cs)
$p(AnO_2A_2)$	Partial pressure of $AnO_2A_2(g)$
$p(AnO_2B_2)$	Partial pressure of $AnO_2B_2(g)$
$p(AnO_2AB)$	Partial pressure of $AnO_2AB(g)$
$r(An^{+n})$	Atomic radii of actinide +n ion

**Nomenclature (cont.)**

$r(Cl^-)$	Atomic radii of chloride ion
$r(F^-)$	Atomic radii of fluoride ion
$r(O^{2-})$	Atomic radii of oxygen ion
$S^\circ(298)$	Standard entropy at 298 K
$S^\circ(T)$	Standard entropy at T
T	Temperature in Kelvin
X	Halide or oxide (O, Cl, F, or OH)
$\Delta G_f^\circ(298)$	Standard free energy of formation at 298 K
$\Delta H_f^\circ(298)$	Standard enthalpy of formation at 298 K
$\Delta S_f^\circ(298)$	Standard entropy of formation at 298 K
$\sigma_A$	Symmetry number of $A_nO_2A_2(g)$
$\sigma_B$	Symmetry number of $A_nO_2B_2(g)$
$\sigma_{AB}$	Symmetry number of $A_nO_2AB(g)$

## 1. Introduction

Known thermodynamic data for uranium vapor species [1-6] show that  $\text{UO}_3(\text{g})$ ,  $\text{UO}_2\text{Cl}_2(\text{g})$ ,  $\text{UO}_2\text{F}_2(\text{g})$ , and  $\text{UO}_2(\text{OH})_2(\text{g})$  are important high-temperature vapor species formed from the volatilization of uranium oxide in the presence of oxygen, chlorine, fluorine, and water vapor. Similar species have not yet been identified for neptunium and americium, but some date exists for plutonium which suggests that  $\text{PuO}_3(\text{g})$  and  $\text{PuO}_2(\text{OH})_2(\text{g})$  are important high-temperature vapor species formed in the presence of oxygen and water vapor [6a]. Considering both the uranium and plutonium data, it is likely that species of the general formulas  $\text{AnO}_3(\text{g})$ ,  $\text{AnO}_2\text{Cl}_2(\text{g})$ ,  $\text{AnO}_2\text{F}_2(\text{g})$ , and  $\text{AnO}_2(\text{OH})_2(\text{g})$  ( $\text{An} = \text{U}, \text{Np}, \text{Pu}, \text{and Am}$ ) are important under conditions where oxygen, water vapor, and halide gases are present. The thermodynamics of all these actinide vapor species are needed in order to make accurate assessments of the amount of actinide volatility that could occur in thermal oxidation treatments of actinide containing wastes, *i.e.* incineration and most incineration alternatives. Actinide volatility is an important factor in assessing the possibility of producing emissions to the atmosphere in a thermal treatment process. Except for the standard enthalpies and free energies of formation, this study provides all the relevant thermodynamic functions for each vapor species that might be important except for the standard enthalpies and free energies of formation.

If accurate thermodynamic functions are available, known vaporization data are best analyzed by treating the data by the third law method to obtain the standard enthalpy of reaction. This treatment allows known volatilization data to be accurately extrapolated well beyond the temperature range of measurement. Thermodynamic functions and constants for the gaseous species can be calculated by the molecular constant method using known molecular constants where available and estimated molecular constants otherwise. For the actinide vapor species considered in this study, most of the molecular constants are unknown. However, reasonable estimates can be made from available data on solid actinides and structurally related vapor species.

It is the purpose of this work to compile reasonable estimates for the molecular constants of the actinide oxide, oxychloride, oxyfluoride, and oxyhydroxide vapor species and to calculate the resulting thermodynamic functions and constants. This information will be useful in later work to interpret actinide oxide vaporization data or to estimate vaporization properties of species for which data are currently unavailable.

## 2. Molecular Constants

The thermodynamic functions of the actinide oxide, oxyhydroxide, oxychloride, and oxyfluoride vapor species can be calculated from the molecular constant method using the formulas given by Lewis, et al. [7] and by Pitzer and Gwinn [8]. The molecular constants which are needed to calculate the thermodynamic functions are the molecular weights, structures, bond lengths, vibrational wave numbers, and electronic transitions. For the oxyhydroxides, internal rotation of the hydroxide groups must also be included.

### 2.1 Molecular Weights

The molecular weights of the gaseous molecules are used to calculate the translational contribution to the thermodynamic functions. The atomic weight of uranium was assumed to be that of natural uranium. For the other actinides, specific isotopes were taken. Neptunium was taken to be  $^{237}\text{Np}$ . Plutonium was taken to be  $^{239}\text{Pu}$ , and americium was taken to be  $^{241}\text{Am}$ .

### 2.2 Structures and Bond Lengths

The structures and bond lengths are used to calculate the rotational contribution to the thermodynamic functions. The structures for the oxides,  $\text{UO}_3(\text{g})$ ,  $\text{PuO}_3(\text{g})$ ,  $\text{NpO}_3(\text{g})$ , and  $\text{AmO}_3(\text{g})$ , were all assumed to be T-shaped with  $\text{C}_{2v}$  symmetry and a symmetry number equal to 2. This is the structure Gabelnick, *et al.* [9] found for  $\text{UO}_3(\text{g})$  from IR matrix isolation studies. The structures of

the actinide oxychlorides, oxyfluorides, and oxyhydroxides were assumed to be tetrahedrally shaped structures with  $C_{2v}$  symmetry and a symmetry number equal to 2. The assumed O-An-O, Cl-An-Cl, F-An-F, and HO-An-OH bond angles are given in Table 1. These were based on known structures and bond angles for  $\text{CrO}_2\text{Cl}_2(\text{g})$  [10],  $\text{CrO}_2\text{F}_2(\text{g})$  [11],  $\text{MoO}_2\text{Cl}_2(\text{g})$  [12],  $\text{WO}_2\text{Cl}_2(\text{g})$  [13], and  $\text{WO}_2\text{F}_2(\text{g})$  [14]. The bond angles in each of the corresponding uranium, neptunium, plutonium, and americium species were assumed to be the same.

The  $\text{U}^{+6}=\text{O}$  bond length of 0.1700 nm was taken to be the same as the  $\text{U}^{+6}=\text{O}$  bond length in  $\text{NaUO}_2(\text{O}_2\text{CCH}_3)_3(\text{s})$  given by Zachariasen and Plettinger [15]. This is the shortest reported +6 uranium-oxygen bond length in a solid mixed oxide containing uranium. The shortest known bond length in the solid would presumably be the closest to the actual  $\text{U}^{+6}=\text{O}$  double bond since +6 uranium-oxygen bonds in solids can be singly bonded or only partially double bonded in character and hence longer. In addition, 0.1700 nm is close to the bond expected based on the known  $\text{U}^{+2}=\text{O}$  bond length in  $\text{UO}(\text{g})$  [16] and the known  $\text{U}^{+2}$  and  $\text{U}^{+6}$  ionic radii [17]. If the  $\text{U}^{+6}=\text{O}$  bond length is estimated by the difference in the ionic sizes of  $\text{U}^{+2}$  and  $\text{U}^{+6}$  given by Ziolkowski [17], then the following  $\text{U}^{+6}=\text{O}$  bond length is obtained:

$$d(\text{U}^{+6}=\text{O}) = d(\text{U}^{+2}=\text{O}) - r(\text{U}^{+2}) + r(\text{U}^{+6}), \text{ nm} \quad (1)$$

$$0.1671 = 0.1838 - 0.1214 + 0.1047$$

which agrees well with the assumed  $\text{U}^{+6}=\text{O}$  bond length of 0.1700 nm. The bond length calculated in eqn (1) is probably a bit shorter since the  $\text{U}^{+6}=\text{O}$  bond strength is less than the  $\text{U}^{+2}=\text{O}$  bond strength. From the standard enthalpies of formation for  $\text{UO}_3(\text{g})$ ,  $\text{UO}(\text{g})$ ,  $\text{U}(\text{g})$ , and  $\text{O}(\text{g})$  reported by Grenthe, *et al.* [18], average  $\text{U}^{+6}=\text{O}$  and  $\text{U}^{+2}=\text{O}$  bond energies are calculated to be 693.2 and 751.7 kJ/mol, respectively.

The  $\text{U}^{+6}-\text{F}$ ,  $\text{Np}^{+6}-\text{F}$ , and  $\text{Pu}^{+6}-\text{F}$  bond lengths of 0.1996, 0.1981, and 0.1971 nm were taken from molecular diffraction data on  $\text{UF}_6(\text{g})$ ,  $\text{NpF}_6(\text{g})$ , and  $\text{PuF}_6(\text{g})$  [19]. The  $\text{U}^{+6}-\text{Cl}$  bond length of 0.2459 nm was estimated from the bond length in  $\text{UCl}_4(\text{g})$  [20], the ionic radii of  $\text{U}^{+6}$  and  $\text{U}^{+4}$  given

by Ziolkowski [17], and the U-F bond lengths in UF<sub>4</sub>(g) [21] and UF<sub>6</sub>(g) [19]. From the ionic radii of uranium given by Ziolkowski, the U<sup>+6</sup>-Cl bond length was calculated by the relationship

$$d(U^{+6}\text{-Cl}) = d(U^{+4}\text{-Cl}) - r(U^{+4}) + r(U^{+6}), \text{ nm} \quad (2)$$

$$0.2450 = 0.2538 - 0.1135 + 0.1047$$

and from the electron diffraction data on UF<sub>4</sub>(g) and UF<sub>6</sub>(g), the U<sup>+6</sup>-Cl bond length was also calculated by the relationship

$$d(U^{+6}\text{-Cl}) = d(U^{+4}\text{-Cl}) - r(U^{+4}\text{-F}) + r(U^{+6}\text{-F}), \text{ nm} \quad (3)$$

$$0.2467 = 0.2538 - 0.2067 + 0.1996.$$

Averaged these yield 0.2459 nm for the estimated bond length of U<sup>+6</sup>-Cl. The U<sup>+6</sup>-OH bond length was calculated from the estimated U<sup>+6</sup>-Cl and the known U<sup>+6</sup>-F bond length and the ionic radii for F<sup>-</sup>, Cl<sup>-</sup>, and O<sup>2-</sup> given by Ziolkowski [17]. Thus,

$$r(U^{+6}\text{-OH}) = r(U^{+6}\text{-F}) - r(F^-) + r(O^{2-}), \text{ nm} \quad (4)$$

$$0.2063 = 0.2055 - 0.0765 + 0.0829$$

and

$$r(U^{+6}\text{-OH}) = r(U^{+6}\text{-Cl}) - r(Cl^-) + r(O^{2-}), \text{ nm} \quad (5)$$

$$0.2045 = 0.2459 - 0.1243 + 0.0829.$$

Averaged these yield 0.2054 nm for the U<sup>+6</sup>-OH bond length.

The bond lengths in the neptunium and plutonium species are based on the bond lengths taken for the uranium species and the known bond lengths in the uranium, neptunium, and plutonium fluorides [19]. To estimate bond lengths in the neptunium and plutonium species, the following relationships were used:

$$d(Np^{+6}\text{-X}) = d(U^{+6}\text{-X}) - 0.015, \text{ nm} \quad (6)$$

and

$$d(Pu^{+6}\text{-X}) = d(U^{+6}\text{-X}) - 0.025, \text{ nm} \quad (7)$$

where X = O, Cl, F, or OH. The bond lengths in the americium species were based on the bond

lengths in the uranium species, the known uranium, neptunium, and plutonium fluorides, and known actinide-oxygen bond distances in alkali-actinide mixed oxides. The unit cell parameters for a number of alkali-actinide mixed oxides of the general formula  $M_2AnO_4$  (where  $M = K, Rb, Cs$  and  $An = U, Np, Pu, Am$ ) are given by Hoekstra and Gerbert [22,23]. These compounds are isostructural with  $K_2NiF_4(s)$ . From this structure, the  $a$  and  $c$  parameters are equal and are given by 2 U-O bonds. The  $c$  parameter has 2 U-O bonds along its axis in addition to other M-An and M-O bonds. Assuming the M-An and M-O bonds are the same through a series of mixed oxides (*i.e.* where only the actinide ions are changed), the relative distances plus an unknown constant for each series of mixed oxides of the An-O bonds are given by

$$d(An=O) + C(M) = a(An,M)/3 + c(An,M)/6. \quad (8)$$

The unit cell parameters for mixed alkali-actinide oxide compounds, the actinide-oxygen bond distance plus an unknown constant, and the actinide-oxygen bond distance relative to the americium-oxygen bond distance are given in Table 2. Using the average difference in the actinide-oxygen bond distance and the americium-oxygen bond distance,  $d(An=O) - d(Am=O)$ , and the known U-F, Np-F, and Pu-F bond distances, the Am-F bond distance was calculated to be 0.1960 nm. For the other americium species, the americium bond length was assumed to be given by the difference in the  $U^{+6}$ -F and  $Am^{+6}$ -F bond lengths and the estimated bond length in the corresponding uranium species. Thus,

$$d(Am^{+6}-X) = d(U^{+6}-X) - 0.036, \text{ nm} \quad (9)$$

where  $X = O, Cl, F$ , or  $OH$ . The estimated bond lengths for each of the actinide oxides, oxychlorides, oxyfluorides, and oxyhydroxides are summarized in Table 3.

### 2.3 Vibrational Energies

The vibrational energies of the fundamental vibrational modes are used to calculate the vibrational contribution to the thermodynamic functions. The vibrational wave numbers for  $UO_3(g)$

are reported by Gabelnick, *et al.* [9] and are given in Table 4. The wave numbers for NpO<sub>3</sub>(g), PuO<sub>3</sub>(g), and AmO<sub>3</sub>(g) were all assumed to be the same as for UO<sub>3</sub>(g). The vibrational wave numbers for UO<sub>2</sub>Cl<sub>2</sub>(g) were based primarily on known vibrational wave numbers for CrO<sub>2</sub>Cl<sub>2</sub>(g) [10], MoO<sub>2</sub>Cl<sub>2</sub>(g) [13], WO<sub>2</sub>Cl<sub>2</sub>(g) [13,24], and UCl<sub>4</sub>(g) [25] and the vibrational wave numbers for UO<sub>2</sub>F<sub>2</sub>(g) were based primarily on known and estimated vibrational wave numbers for CrO<sub>2</sub>F<sub>2</sub>(g) [11], MoO<sub>2</sub>F<sub>2</sub>(g) [26], WO<sub>2</sub>F<sub>2</sub>(g) [26], and UF<sub>4</sub>(g) [27]. Vibrational wave numbers for UO<sub>2</sub>(OH)<sub>2</sub>(g) were based primarily on the values taken for UO<sub>2</sub>Cl<sub>2</sub>(g) and UO<sub>2</sub>F<sub>2</sub>(g) and on known vibrational wave numbers in UO<sub>3</sub>.H<sub>2</sub>O(s) and UO<sub>3</sub>.0.8H<sub>2</sub>O(s) [28]. Known and estimated vibrational wave numbers for the chromium, molybdenum, and tungsten oxychlorides and oxyfluorides are summarized in Table 5.

For UO<sub>2</sub>Cl<sub>2</sub>(g), UO<sub>2</sub>F<sub>2</sub>(g), and UO<sub>2</sub>(OH)<sub>2</sub>(g), the U-O symmetric and anti-symmetric stretching vibrations of 831 and 916 cm<sup>-1</sup> were taken from the same vibrations in UO<sub>2</sub>Cl<sub>4</sub><sup>2-</sup> given by Denning [29].

For UO<sub>2</sub>Cl<sub>2</sub>(g), the U-Cl symmetric and anti-symmetric stretching vibrations of 324 and 348 cm<sup>-1</sup> were taken from the same vibrations in UCl<sub>4</sub>(g) given by Bazhanov, *et al.* [25].

For UO<sub>2</sub>F<sub>2</sub>(g), the U-F symmetric and anti-symmetric stretching vibrations of 541 and 605 cm<sup>-1</sup> were taken from the same vibrations in UF<sub>4</sub>(g) given by Bukhmarina, *et al.* [27].

For UO<sub>2</sub>(OH)<sub>2</sub>(g), the U-OH symmetric and anti-symmetric stretching vibrations of 439 and 471 cm<sup>-1</sup> were taken from similar vibrations in UO<sub>3</sub>.0.8H<sub>2</sub>O(s) given by Deane [28].

In UO<sub>2</sub>Cl<sub>2</sub>(g), the O-U-O bending vibration of 340 cm<sup>-1</sup> was taken to be an average of the corresponding vibrations in MoO<sub>2</sub>Cl<sub>2</sub>(g) and WO<sub>2</sub>Cl<sub>2</sub>(g), the O-U-O rocking vibration of 214 cm<sup>-1</sup> was taken to be an average of the corresponding vibrations in CrO<sub>2</sub>Cl<sub>2</sub>(g), MoO<sub>2</sub>Cl<sub>2</sub>(g), and WO<sub>2</sub>Cl<sub>2</sub>(g), the Cl-U-Cl bending vibration of 108 cm<sup>-1</sup> was taken to be an average of corresponding vibrations in UCl<sub>4</sub>(g), CrO<sub>2</sub>Cl<sub>2</sub>(g), and MoO<sub>2</sub>Cl<sub>2</sub>(g). The Cl-U-Cl rocking vibration of 262 cm<sup>-1</sup> was taken to be an average of the corresponding vibrations in CrO<sub>2</sub>Cl<sub>2</sub>(g) and MoO<sub>2</sub>Cl<sub>2</sub>(g). The twisting

vibration of  $172\text{ cm}^{-1}$  was taken to be an average of the corresponding vibrations in  $\text{UCl}_4(\text{g})$ ,  $\text{CrO}_2\text{Cl}_2(\text{g})$ , and  $\text{MoO}_2\text{Cl}_2(\text{g})$  where the vibration in  $\text{MoO}_2\text{Cl}_2(\text{g})$  is weighted double since the twisting vibration in  $\text{WO}_2\text{Cl}_2(\text{g})$  is not known. In  $\text{UO}_2\text{F}_2(\text{g})$ , the O-U-O bending vibration of  $364\text{ cm}^{-1}$  was taken to be an average of the corresponding vibrations in  $\text{CrO}_2\text{F}_2(\text{g})$  and  $\text{MoO}_2\text{F}_2(\text{g})$ . The O-U-O rocking vibration of  $235\text{ cm}^{-1}$  was taken to be an average of the corresponding vibrations in  $\text{MoO}_2\text{F}_2(\text{g})$  and  $\text{WO}_2\text{F}_2(\text{g})$ . The F-U-F bending vibration of  $199\text{ cm}^{-1}$  was taken to be the same as the corresponding vibration in  $\text{MoO}_2\text{F}_2(\text{g})$ . The F-U-F rocking vibration of  $265\text{ cm}^{-1}$  was taken to be the same as the corresponding vibration in  $\text{WO}_2\text{F}_2(\text{g})$ , and the twisting vibration of  $259\text{ cm}^{-1}$  was taken to be the same as the corresponding vibration in  $\text{CrO}_2\text{F}_2(\text{g})$ .

In  $\text{UO}_2(\text{OH})_2(\text{g})$ , the O-U-O bending and rocking vibrations of  $352$  and  $225\text{ cm}^{-1}$ , the HO-U-OH bending and rocking vibrations of  $154$  and  $264\text{ cm}^{-1}$ , and the twisting vibration of  $215\text{ cm}^{-1}$  were all taken to be an average of the corresponding vibrations in  $\text{UO}_2\text{Cl}_2(\text{g})$  and  $\text{UO}_2\text{F}_2(\text{g})$ . The O-H symmetric and anti-symmetric stretching vibrations were both taken to be  $3370\text{ cm}^{-1}$  and the U-O-H symmetric and anti-symmetric bending vibrations were taken to be  $874$  and  $986\text{ cm}^{-1}$ . These wave numbers were based upon similar vibrations for  $\text{UO}_3\cdot\text{H}_2\text{O}(\text{s})$  found by Deane [28].

The vibrational wave numbers assumed for  $\text{UO}_2\text{Cl}_2(\text{g})$ ,  $\text{UO}_2\text{F}_2(\text{g})$ , and  $\text{UO}_2(\text{OH})_2(\text{g})$  are summarized in Table 6. Vibrational wave numbers for the corresponding Np, Pu, and Am species were taken to be identical to the U species.

#### *2.4 Electronic Transitions*

The electronic energy levels are used to calculate the electronic contribution to the thermodynamic functions. Estimating this contribution to the thermodynamic functions was the most difficult for the actinide vapor species because there are no spectroscopic data available for any of the +6 actinide vapor species. One common method for estimating the electronic contribution is to use the atomic states model. In this approach, the electronic states for the +6

actinide ion would be used as an approximation for the electronic states of the actinide +6 gaseous molecule. Unfortunately, no spectroscopic data are available for the +6 gaseous actinide ions. However, spectroscopic data for the +1, +2 and +3 actinide ions are reported by Brewer [30]. Based on his work the ground states of the +6 actinide ions are inferred from the isoelectronic +3 actinide ions. Using this approach the ground state configurations are  $f^0$  for  $U^{+6}(g)$ ,  $f^1 (^2F_{5/2})$  for  $Np^{+6}(g)$ ,  $f^2 (^3H_4)$  for  $Pu^{+6}(g)$ , and  $f^3 (^4I_{9/2})$  for  $Am^{+6}(g)$ .

Although there are no spectroscopic data for the actinide vapor species or +6 gaseous actinide ions, there are spectroscopic data for the actanyl ions ( $AnO_2^{2+}$ ) in solids and solutions. These spectroscopic data can be used to estimate the electronic contributions to the thermodynamic functions for each of the actinide vapor species. The first excited energy level in  $UO_2^{2+}$  is known to be greater than  $20,000\text{ cm}^{-1}$  [31]. This is large enough such that the electronic contribution to the thermodynamic functions for the +6 uranium vapor species is essentially zero and is therefore neglected in the thermodynamic functions calculated for all the uranium vapor species. The energy levels in  $NpO_2^{2+}$  were taken from Rozov and Mironov [32]. The energy levels in  $PuO_2^{2+}$  were taken from Eisenstein and Pryce [33], and the energy levels in  $AmO_2^{2+}$  were taken from Varga, *et al.* [34]. Energy levels in  $NpO_2^{2+}$ ,  $PuO_2^{2+}$ , and  $AmO_2^{2+}$  are summarized in Table 7. These energy levels can be assumed to be approximately the same as in the actinide vapor species. However, the T-shaped oxides and the tetrahedrally shaped orientation of the oxychlorides, oxyfluorides, and oxyhydroxides will result in a splitting of the energy levels relative to the  $NpO_2^{2+}$ ,  $PuO_2^{2+}$ , and  $AmO_2^{2+}$  ions which are all linear shaped ions and show no measurable splitting in energy levels. The splitting of the ground state will have the greatest effect on the calculated thermodynamic parameters, whereas splitting of higher energy states will have a lesser and essentially insignificant effect on the calculated thermodynamic parameters and was therefore neglected. However, ground state splitting can be significant in these calculations. The energy splitting in the ground state of +6 actinide species was approximated using low lying energy levels in  $UF_4(s)$ ,  $NpF_4(s)$ , and  $PuF_4(s)$

[35]. Data from isoelectronic and isostructural gaseous or even liquid species would have been more desirable, but this was the only relevant data that was found. The solids,  $\text{UF}_4(\text{s})$  and  $\text{NpF}_4(\text{s})$ , are isoelectronic with the +6 Pu and Am species, respectively. However, the fluorine atoms are eight coordinated in an antiprismatic structure around the central actinide ion rather than tetrahedrally oriented as most of the species considered in this study. The energy level splitting of the ground state in the plutonium vapor species was taken from  $\text{UF}_4(\text{s})$  and the energy level splitting of the ground state in the americium vapor species was taken from  $\text{NpF}_4(\text{s})$ . The energy level splitting of the ground state in the +6 neptunium vapor species was taken from the estimated splitting of the ground state in  $\text{PaF}_4(\text{s})$ . This splitting was assumed to be similar to  $\text{NpF}_4(\text{s})$ . Ground state is split into three energy levels each with a degeneracy of 2. Absolute ground state is  $0 \text{ cm}^{-1}$ . Based on the data for  $\text{NpF}_4(\text{s})$ , the intermediate state will be around  $700 \text{ cm}^{-1}$  and the high energy state will be around  $1200 \text{ cm}^{-1}$ . Actual levels selected were  $735 \text{ cm}^{-1}$  and  $1188 \text{ cm}^{-1}$  for the intermediate and high energy levels, respectively. The energy levels substituted for the ground state of the actynyl ions are given in Table 8. These energy levels along with those from Table 7 (excluding the ground state) are then used to calculate the electronic contribution to each of the actinide vapor species.

Taking the ground states as split into the energy states given in Table 8 effects primarily the entropies and the free energy functions at lower temperatures. At 298 K, for example, the electronic contribution to the entropies of the +6 Np, Pu, and Am species are calculated to be 7.00, 7.74, and 9.42 J/mol-K, respectively. Taking the ground states given in Table 7, however, the electronic contributions to the entropies at 298 K of the +6 Np, Pu, and Am species are calculated to be 14.90, 18.27, and 19.14 J/mol-K, respectively. It is known that the atomic states model by itself, which assumes no splitting of the energy levels of the gaseous ion, will over estimate the entropy and free energy of the species. Green discussed this previously [40]. The assumption of splitting of the ground state reduces the calculated entropy and free energy resulting in what should

be a more accurate calculation. Higher energy levels will also be split relative to the free ion, the impact at higher energies of energy level splitting on the calculated thermodynamic functions is minimal.

### *2.5 Internal Rotation Parameters*

For the oxyhydroxides, the contribution to the thermodynamic functions from the rotation of the hydroxide molecule must also be considered. The contribution to the thermodynamic functions of the internal rotation of hydroxide groups can be calculated by the method of Pitzer and Gwinn [8]. Since the potential barrier to rotation is small, simplified equations are used herein to calculate the contribution to the thermodynamic functions. These are the same functions as those used to calculate the hydroxide internal rotation contribution to the thermodynamic functions for the gaseous chromium oxyhydroxides [36].

The moment of inertia for the internal rotation of one hydroxide group,  $1.42 \times 10^{-47}$  kg m<sup>2</sup>, can be calculated from the assumed O-H bond length of 0.097 nm and U-O-H bond angle of 108.5° which were taken from H<sub>2</sub>SO<sub>4</sub>(g) [37]. The symmetry number of rotation was taken to be 1 for each hydroxide group and the potential barrier for rotation was estimated to be 3.0 kJ/mol. The potential barrier for rotation in H<sub>2</sub>SO<sub>4</sub>(g) and HClO<sub>4</sub>(g) are given by Giguere and Savoie [38,39] to be 5.4 and 6.7 kJ/mol, respectively. Since the An-OH bond lengths are considerably longer than the S-OH or Cl-OH bond lengths, the potential barrier for rotation was expected to be much less in the actinide oxyhydroxides than in either H<sub>2</sub>SO<sub>4</sub>(g) or HClO<sub>4</sub>(g). To give an idea of the error induced by this estimate, the standard entropies at 298 K calculated for a hydroxide group with potential barriers for rotation of 5.4, 3.0, and 0.0 kJ/mole are 16.67, 17.97, and 18.68 J/mol-K, respectively.

## **3. Thermodynamic Functions**

### *3.1 Oxides, Oxyhydroxides, Oxychlorides, and Oxyfluorides*

For the molecular constants given above, the thermodynamic functions for the actinide oxide, oxyhydroxide, oxychloride, and oxyfluoride vapor species were then calculated. Thermodynamic functions for the uranium, neptunium, plutonium, and americium species are given in Tables 9 to 12, 13 to 16, 17 to 20, and 21 to 24, respectively. For each table the heat capacities are fit to an equation of the form

$$C_p(T) = A + Bx10^{-3}T + Cx10^5T^{-2} + Dx10^{-6}T^2, \text{ J/mol-K} \quad (10)$$

and the free energy functions are fit to an equation of the form

$$\begin{aligned} -(G^\circ - H^\circ(298))/T &= A + Bx10^{-3}T + Cx10^{-6}T^2 + Dx10^{-9}T^3 + \\ &Ex10^{-12}T^4, \text{ J/mol-K} \end{aligned} \quad (11)$$

over temperature ranges of 298 to 1000 K and 1000 to 3000 K.

A previous calculation of  $S^\circ(298)$  for  $\text{UO}_3(\text{g})$  by Green [40] is very close to that calculated herein. As can be seen in Table 25, however, the entropies deviate at higher temperatures. This results from the estimated additional electronic contribution Green includes for  $\text{UO}_3(\text{g})$  which was not included herein. The  $S^\circ(298)$  value for  $\text{UO}_2\text{Cl}_2(\text{g})$  calculated herein differs appreciably from that calculated by Grenthe, *et al.* [18]. Since Grenthe, *et al.* do not report the molecular constants they used, the reason for the discrepancy is not apparent. The entropies calculated herein for  $\text{UO}_2\text{F}_2(\text{g})$  also differ appreciably from those calculated by Lau, *et al.* [4]. The difference arises primarily because significantly different vibrational wave numbers are used herein.

### 3.2 Mixed Vapor Species

In addition to the oxychlorides, oxyfluorides, and oxyhydroxides of uranium, neptunium, plutonium, and americium, a number of mixed species are possible. In particular these are species of the formulas,  $\text{AnO}_2\text{ClOH}(\text{g})$ ,  $\text{AnO}_2\text{FOH}(\text{g})$ , and  $\text{AnO}_2\text{FCl}(\text{g})$ , where  $\text{An} = \text{U}, \text{Np}, \text{Pu}$ , or  $\text{Am}$ . In a previous paper on chromium vapor species [41], it was suggested that these vapor species are only important when the counterpart species are present in about equal concentrations. Using the same

arguments as discussed in a previous paper, the thermodynamics of these species can be estimated from the reaction



where A and B are equal to Cl, F, or OH. The equilibrium constant is given by

$$K_{\text{eq}} = p(\text{AnO}_2\text{AB}) / p(\text{AnO}_2\text{A}_2)^{1/2} p(\text{AnO}_2\text{B}_2)^{1/2} \quad (13)$$

or

$$K_{\text{eq}} = \sigma_A^{1/2} \sigma_B^{1/2} / \sigma_{\text{AB}} \quad (14)$$

where  $\sigma_A$ ,  $\sigma_B$ , and  $\sigma_{\text{AB}}$  are the symmetry numbers of  $\text{AnO}_2\text{A}_2(\text{g})$ ,  $\text{AnO}_2\text{B}_2(\text{g})$ , and  $\text{AnO}_2\text{AB}(\text{g})$ , respectively. An equilibrium constant equal to 2 is calculated constant given a symmetry number of 1 for  $\text{AnO}_2\text{AB}(\text{g})$  and symmetry numbers equal to 2 for  $\text{AnO}_2\text{A}_2(\text{g})$  and  $\text{AnO}_2\text{B}_2(\text{g})$ . Thus, the enthalpy of reaction,  $\Delta H^\circ_r(298)$ , is equal to zero and the entropy of reaction,  $\Delta S^\circ_r(298)$ , is equal to  $R \ln 2$ .

#### 4. Conclusions

The thermodynamic functions,  $C_p^\circ$  and  $-(G^\circ - H^\circ(298))/T$ , and the thermodynamic constants,  $S^\circ(298)$  and  $H^\circ(298) - H^\circ(0)$ , have been calculated as a function of temperature for the +6 actinide oxide, oxyhydroxide, oxychloride, and oxyfluoride vapor species. For each species the only remaining thermodynamic constant needed is the standard enthalpy,  $\Delta H_f^\circ(298)$ , or free energy of formation,  $\Delta G_f^\circ(298)$ . Either constant can be evaluated from known vaporization data using the thermodynamic functions given herein or estimated from bond energy correlations if experimental data are unavailable.

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Table 1. Estimated bond angles in  $\text{AnO}_2\text{Cl}_2(\text{g})$ ,  $\text{AnO}_2\text{F}_2(\text{g})$ , and  $\text{AnO}_2(\text{OH})_2(\text{g})$  derived from known bond angles in the chromium, molybdenum, and tungsten oxychlorides and oxyfluorides.

species	angle	$\text{M} = \text{Cr}$	$\text{M} = \text{Mo}$	$\text{M} = \text{W}$	$\text{M} = \text{U, Np, Pu, Am}$
$\text{MO}_2\text{Cl}_2$	O-M-O	108.5	106.3	108	106.5
	Cl-M-Cl	113.2	113.9	---	113.6
$\text{MO}_2\text{F}_2$	O-M-O	107.8	---	97	106.5
	F-M-F	111.9	---	111	111.5
$\text{MO}_2(\text{OH})_2$	O-M-O	---	---	---	106.5
	HO-M-OH	---	---	---	112.6

Table 2. Relative bond lengths in actinide oxides

$$d(An^{+6}=O) + C(M) = a(An,M)/3 + c(An,M)/6$$

compound	a(An,M) (nm)	c(An,M) (nm)	d(An=O) + C(M) (nm)	d(An=O) - d(An=O) (nm)
K <sub>2</sub> UO <sub>4</sub>	0.4333	1.317	0.3639	0.0035
K <sub>2</sub> NpO <sub>4</sub>	0.4299	1.315	0.3625	0.0021
K <sub>2</sub> PuO <sub>4</sub>	0.4298	1.307	0.3611	0.0007
K <sub>2</sub> AmO <sub>4</sub>	0.4286	1.305	0.3604	0.0000
Rb <sub>2</sub> UO <sub>4</sub>	0.4354	1.386	0.3761	0.0037
Rb <sub>2</sub> NpO <sub>4</sub>	0.4325	1.385	0.3750	0.0026
Rb <sub>2</sub> PuO <sub>4</sub>	0.4323	1.374	0.3731	0.0007
Rb <sub>2</sub> AmO <sub>4</sub>	0.4316	1.371	0.3724	0.0000
Cs <sub>2</sub> UO <sub>4</sub>	0.43917	1.4803	0.3931	0.0035
Cs <sub>2</sub> NpO <sub>4</sub>	0.4367	1.478	0.3919	0.0023
Cs <sub>2</sub> PuO <sub>4</sub>	0.4368	1.471	0.3908	0.0012
Cs <sub>2</sub> AmO <sub>4</sub>	0.4364	1.465	0.3896	0.0000

Table 3. Estimated bond lengths for hexavalent uranium oxide, oxychloride, oxyfluoride, and oxyhydroxide molecules.

species	r(M=O) (nm)	r(M-Cl) (nm)	r(M-F) (nm)	r(M-OH) (nm)
U	0.1700	0.2459	0.1996	0.2054
Np	0.1685	0.2444	0.1981	0.2039
Pu	0.1675	0.2434	0.1971	0.2029
Am	0.1664	0.2423	0.1960	0.2018

Table 4. Vibrational wave numbers for  $\text{UO}_3(\text{g})$ . Vibrational wave numbers for the corresponding Np, Pu, and Am oxides were taken to be identical to those of  $\text{UO}_3(\text{g})$ .

symmetry	vibration	$\text{UO}_3(\text{g})$ ( $\text{cm}^{-1}$ )
$A_1$	per. str.	843.5
$A_1$	sym. str.	745.6
$A_1$	bend	186.2
$B_1$	asym. str.	852.6
$B_1$	defor.	211.6
$B_2$	out-plane	151.5

Table 5. Comparison of vibrational wave numbers for  $\text{MO}_2\text{Cl}_2(\text{g})$  and  $\text{MO}_2\text{F}_2(\text{g})$  where M = Cr, Mo, W.

symmetry	vibration	$\text{CrO}_2\text{Cl}_2$ (cm $^{-1}$ )	$\text{MoO}_2\text{Cl}_2$ (cm $^{-1}$ )	$\text{WO}_2\text{Cl}_2$ (cm $^{-1}$ )
A <sub>1</sub>	(M=O)	991	997.4	1014.9
B <sub>1</sub>	(M=O)	1002	971.4	977.8
A <sub>1</sub>	(M-Cl)	470	434.0	426.0
B <sub>2</sub>	(M-Cl)	502.7	450.4	431
A <sub>1</sub>	(MO <sub>2</sub> )	355.8	339	340
A <sub>1</sub>	(MCl <sub>2</sub> )	139.2	113	---
B <sub>1</sub>	(MO <sub>2</sub> )	212	211	220
B <sub>2</sub>	(MCl <sub>2</sub> )	257	267	---
A <sub>2</sub>	twist	224	196	---
symmetry	vibration	$\text{CrO}_2\text{F}_2$ (cm $^{-1}$ )	$\text{MoO}_2\text{F}_2$ (cm $^{-1}$ )	$\text{WO}_2\text{F}_2$ (cm $^{-1}$ )
A <sub>1</sub>	(M=O)	1006	987	(998)
B <sub>1</sub>	(M=O)	1016	1012	(1001)
A <sub>1</sub>	(M-F)	727	692	(709)
B <sub>2</sub>	(M-F)	789	705	(698)
A <sub>1</sub>	(MO <sub>2</sub> )	364	365	(350)
A <sub>1</sub>	(MF <sub>2</sub> )	208	(199)	(202)
B <sub>1</sub>	(MO <sub>2</sub> )	274	(243)	(226)
B <sub>2</sub>	(MF <sub>2</sub> )	304	275	(265)
A <sub>2</sub>	twist	259	(260)	(261)

Numbers in parenthesis are estimated in ref [26].

Table 6. Estimated vibrational wave numbers for  $\text{UO}_2\text{Cl}_2(\text{g})$ ,  $\text{UO}_2\text{F}_2(\text{g})$ , and  $\text{UO}_2(\text{OH})_2(\text{g})$ . Vibrational wave numbers for the corresponding Np, Pu, and Am species are taken to be identical to those for the U species.

symmetry	vibration	$\text{UO}_2\text{Cl}_2$ ( $\text{cm}^{-1}$ )	$\text{UO}_2\text{F}_2$ ( $\text{cm}^{-1}$ )	$\text{UO}_2(\text{OH})_2$ ( $\text{cm}^{-1}$ )
$A_1$	(U=O)	831.0	831.0	831.0
$B_1$	(U=O)	916.0	916.0	916.0
$A_1$	(U-X)	323.5	541.0	439.0
$B_2$	(U-X)	348.5	605.0	471.0
$A_1$	( $\text{UO}_2$ )	339.5	364.5	352.0
$A_1$	( $\text{UX}_2$ )	108.3	199.4	153.9
$B_1$	( $\text{UO}_2$ )	214.3	234.9	224.6
$B_2$	( $\text{UX}_2$ )	262.0	265.4	263.7
$A_2$	twist	171.5	259.0	215.3
$A_1$	(O-H)			3370
$B_1$	(O-H)			3370
$A_1$	(U-O-H)			874.0
$B_1$	(U-O-H)			986.0

Table 7. Energy levels in  $\text{NpO}_2^{2+}$ ,  $\text{PuO}_2^{2+}$ , and  $\text{AmO}_2^{2+}$ .

term	$\text{NpO}_2^{2+}$	$\text{PuO}_2^{2+}$	$\text{AmO}_2^{2+}$	term	g	E( $\text{cm}^{-1}$ )
$\Phi_{5/2}^a$	6	0.0	$^3\text{H}_4$	9	0.0	$^4\text{I}_{9/2}$
$\Delta_{3/2}$	4	1105.9	$\Sigma_0$	1	2445	$^4\text{I}_{11/2}$
$\Delta_{5/2}$	6	6459.0	$\text{H}_1$	3	4258	$^4\text{F}_{3/2}$
$\Phi_{7/2}$	8	9420.2	$^3\text{H}_5$	11	7133	$^2\text{G}_{9/2}$
$\Pi_{1/2}$	2	17843.6	$^3\text{H}_0$	1	10157	$^4\text{G}_{5/2}$
$\Pi_{3/2}$	4	20616.2	$\Sigma_1$	3	10489	$^4\text{I}_{13/2}$
			$^3\text{H}_0$	1	10640	$^2\text{G}_{7/2}$
			$^3\text{H}_2$	5	11892	$^4\text{F}_{5/2}$
			$^3\text{H}_6$	13	12862	$^4\text{F}_{15/2}$
			$^3\text{H}_6$	13	12866	$^4\text{G}_{7/2}$
			$^1\Gamma_4$	9	15649	$^2\text{K}_{13/2}$
			$\Sigma_0$	1	15980	
			$\Sigma_1$	3	17877	
			$^3\Gamma_3$	7	19080	
			$^3\Gamma_3$	7	19086	
			$\Sigma_0$	1	19780	
			$^3\Phi_2$	5	21253	
			$^1\text{H}_5$	11	21885	
			$\Pi_1$	3	23063	
			$\Delta_2$	5	23153	
			$^3\Gamma_4$	9	24527	
			$^1\text{I}_6$	13	24780	
			$^1\text{I}_6$	13	24781	
			$^3\Delta_1$	3	24917	

<sup>a</sup>For the molecular constant calculation, the ground state energy levels are assumed to be split into the energy levels given in Table 8.

Table 8. Assumed splitting of ground state energy levels in +6 neptunium, plutonium, and americium oxides, oxyhydroxides, oxychlorides, and oxyfluorides.

term	Np(+6)		term	Pu(+6)		term	Am(+6)	
	g	E(cm <sup>-1</sup> )		g	E(cm <sup>-1</sup> )		g	E(cm <sup>-1</sup> )
<sup>2</sup> F <sub>5/2</sub>	2	0.0	<sup>3</sup> H <sub>4</sub>	1	0.0	<sup>4</sup> I <sub>9/2</sub>	2	0.0
	2	735		1	10.7		2	470
	2	1188		1	557		2	783
				1	648		2	1126
				1	1132		2	1284
				1	1182			
				1	1436			
				1	1773			
				1	1775			

Table 9. Thermodynamic functions for UO<sub>3</sub>(g). (p° = 1 bar)

T (K)	S°(T) (J/mol-K)	H°(T)-H°(298) (kJ/mol)	C <sub>p</sub> (T) (J/mol-K)	-(G°(T)-H°(298))/T (J/mol-K)
298.15	308.683	0.000	64.542	308.683
300	309.083	0.120	64.662	308.684
400	328.477	6.874	70.092	311.292
500	344.536	14.077	73.721	316.381
600	358.204	21.578	76.125	322.241
700	370.069	29.277	77.755	328.245
800	380.530	37.113	78.895	334.140
900	389.873	45.045	79.717	339.822
1000	398.305	53.049	80.327	345.256
1100	405.984	61.106	80.790	350.433
1200	413.029	69.204	81.149	355.360
1300	419.536	77.333	81.433	360.049
1400	425.580	85.488	81.661	364.517
1500	431.220	93.664	81.847	368.778
1600	436.508	101.857	82.000	372.847
1700	441.483	110.063	82.128	376.740
1800	446.180	118.282	82.236	380.468
1900	450.629	126.510	82.327	384.045
2000	454.854	134.747	82.406	387.481
2100	458.876	142.991	82.473	390.785
2200	462.714	151.241	82.532	393.968
2300	466.384	159.497	82.584	397.038
2400	469.900	167.757	82.629	400.001
2500	473.274	176.022	82.669	402.865
2600	476.517	184.291	82.705	405.636
2700	479.639	192.563	82.736	408.319
2800	482.648	200.838	82.765	410.920
2900	485.553	209.116	82.790	413.444
3000	488.360	217.396	82.813	415.895

T = 298 to 1000 K

$$C_p(T) = 64.452 + 31.700 \times 10^{-3} T - 7.147 \times 10^5 T^{-2} - 15.185 \times 10^{-6} T^2$$

$$-(G^\circ(T)-H^\circ(298))/T = 330.489 - 191.012 \times 10^{-3} T + 520.007 \times 10^{-6} T^2 - 464.858 \times 10^{-9} T^3 + 150.653 \times 10^{-12} T^4$$

T = 1000 to 3000 K

$$C_p(T) = 82.730 + 0.245 \times 10^{-3} T - 26.112 \times 10^5 T^{-2} - 0.040 \times 10^{-6} T^2$$

$$-(G^\circ-H^\circ(298))/T = 279.403 + 81.013 \times 10^{-3} T - 16.7622 \times 10^{-6} T^2 + 1.6426 \times 10^{-9} T^3$$

Table 10. Thermodynamic functions for UO<sub>2</sub>Cl<sub>2</sub>(g). (p° = 1 bar)

T (K)	S°(T) (J/mol-K)	H°(T)-H°(298) (kJ/mol)	C <sub>p</sub> (T) (J/mol-K)	-(G°(T)-H°(298))/T (J/mol-K)
298.15	352.359	0.000	88.757	352.359
300	352.909	0.164	88.902	352.361
400	379.395	9.386	95.016	355.931
500	401.035	19.090	98.790	362.854
600	419.276	29.099	101.212	370.777
700	435.007	39.306	102.829	378.855
800	448.816	49.649	103.952	386.755
900	461.108	60.086	104.758	394.346
1000	472.178	70.593	105.353	401.585
1100	482.241	81.152	105.805	408.467
1200	491.463	91.751	106.154	415.004
1300	499.971	102.380	106.430	421.217
1400	507.867	113.035	106.651	427.128
1500	515.232	123.709	106.832	432.759
1600	522.131	134.400	106.980	438.131
1700	528.621	145.105	107.104	443.265
1800	534.746	155.820	107.208	448.179
1900	540.545	166.546	107.297	452.889
2000	546.050	177.279	107.373	457.411
2100	551.291	188.020	107.439	461.757
2200	556.290	198.767	107.496	465.941
2300	561.070	209.519	107.546	469.974
2400	565.648	220.276	107.589	473.866
2500	570.040	231.037	107.628	477.626
2600	574.262	241.801	107.663	481.262
2700	578.326	252.569	107.693	484.782
2800	582.243	263.340	107.721	488.193
2900	586.024	274.113	107.746	491.502
3000	589.677	284.889	107.768	494.714

T = 298 to 1000 K

$$C_p(T) = 92.149 + 26.902 \times 10^{-3} T - 9.152 \times 10^5 T^{-2} - 12.846 \times 10^{-6} T^2$$

$$-(G^\circ(T) - H^\circ(298))/T = 381.873 - 259.583 \times 10^{-3} T + 709.480 \times 10^{-6} T^2 - 637.367 \times 10^{-9} T^3 + 207.216 \times 10^{-12} T^4$$

T = 1000 to 3000 K

$$C_p(T) = 107.722 + 0.215 \times 10^{-3} T - 25.511 \times 10^5 T^{-2} - 0.035 \times 10^{-6} T^2$$

$$-(G^\circ(T) - H^\circ(298))/T = 313.714 + 108.510 \times 10^{-3} T - 22.8429 \times 10^{-6} T^2 + 2.2634 \times 10^{-9} T^3$$

Table 11. Thermodynamic functions for  $\text{UO}_2\text{F}_2(\text{g})$ . ( $p^\circ = 1 \text{ bar}$ )

T (K)	$S^\circ(T)$ (J/mol-K)	$H^\circ(T) - H^\circ(298)$ (kJ/mol)	$C_p(T)$ (J/mol-K)	$-(G^\circ(T) - H^\circ(298))/T$ (J/mol-K)
298.15	327.049	0.000	83.122	327.049
300	327.564	0.154	83.310	327.051
400	352.719	8.917	91.293	330.426
500	373.660	18.311	96.201	337.038
600	391.497	28.099	99.329	344.666
700	406.974	38.142	101.406	352.486
800	420.615	48.359	102.842	360.166
900	432.790	58.697	103.869	367.571
1000	443.775	69.124	104.627	374.652
1100	453.775	79.616	105.200	381.397
1200	462.949	90.159	105.644	387.816
1300	471.419	100.742	105.993	393.925
1400	479.285	111.356	106.274	399.745
1500	486.625	121.995	106.502	405.295
1600	493.504	132.655	106.690	410.595
1700	499.977	143.332	106.846	415.664
1800	506.088	154.023	106.978	420.520
1900	511.875	164.727	107.090	425.177
2000	517.371	175.441	107.186	429.651
2100	522.602	186.163	107.269	433.953
2200	527.594	196.894	107.341	438.097
2300	532.367	207.631	107.404	442.093
2400	536.940	218.374	107.459	445.950
2500	541.327	229.123	107.508	449.678
2600	545.545	239.876	107.551	453.285
2700	549.604	250.633	107.590	456.777
2800	553.518	261.394	107.625	460.163
2900	557.295	272.158	107.656	463.448
3000	560.945	282.925	107.684	466.637

 $T = 298 \text{ to } 1000 \text{ K}$ 

$$C_p(T) = 87.917 + 34.295 \times 10^{-3} T - 12.081 \times 10^5 T^{-2} - 16.460 \times 10^{-6} T^2$$

$$-(G^\circ(T) - H^\circ(298))/T = 355.956 - 249.485 \times 10^{-3} T + 678.093 \times 10^{-6} T^2 - 605.694 \times 10^{-9} T^3 + 196.174 \times 10^{-12} T^4$$

 $T = 1000 \text{ to } 3000 \text{ K}$ 

$$C_p(T) = 107.660 + 0.251 \times 10^{-3} T - 32.466 \times 10^5 T^{-2} - 0.041 \times 10^{-6} T^2$$

$$-(G^\circ(T) - H^\circ(298))/T = 288.819 + 105.620 \times 10^{-3} T - 21.8788 \times 10^{-6} T^2 + 2.1451 \times 10^{-9} T^3$$

Table 12. Thermodynamic functions for  $\text{UO}_2(\text{OH})_2(\text{g})$ . ( $p^\circ = 1 \text{ bar}$ )

T (K)	$S^\circ(T)$ (J/mol-K)	$H^\circ(T) - H^\circ(298)$ (kJ/mol)	$C_p(T)$ (J/mol-K)	$-(G^\circ(T) - H^\circ(298))/T$ (J/mol-K)
298.15	370.005	0.000	100.884	370.005
300	370.630	0.187	101.086	370.007
400	401.045	10.781	110.239	374.092
500	426.361	22.138	116.506	382.085
600	448.013	34.020	120.899	391.312
700	466.907	46.282	124.196	400.791
800	483.670	58.838	126.852	410.123
900	498.745	71.639	129.106	419.146
1000	512.451	84.650	131.076	427.801
1100	525.028	97.847	132.823	436.076
1200	536.653	111.208	134.380	443.979
1300	547.465	124.717	135.770	451.529
1400	557.573	138.357	137.010	458.746
1500	567.064	152.115	138.117	465.654
1600	576.010	165.977	139.104	472.275
1700	584.470	179.932	139.986	478.628
1800	592.494	193.971	140.773	484.733
1900	600.125	208.084	141.478	490.607
2000	607.398	222.264	142.109	496.266
2100	614.345	236.504	142.676	501.725
2200	620.995	250.797	143.186	506.996
2300	627.370	265.139	143.645	512.092
2400	633.492	279.525	144.061	517.024
2500	639.381	293.950	144.437	521.801
2600	645.053	308.411	144.778	526.433
2700	650.522	322.905	145.089	530.928
2800	655.804	337.428	145.372	535.294
2900	660.910	351.978	145.631	539.538
3000	665.851	366.553	145.868	543.667

 $T = 298 \text{ to } 1000 \text{ K}$ 

$$C_p(T) = 101.089 + 48.976 \times 10^{-3} T - 11.786 \times 10^5 T^{-2} - 17.909 \times 10^{-6} T^2$$

$$-(G^\circ(T) - H^\circ(298))/T = 404.265 - 299.689 \times 10^{-3} T + 814.689 \times 10^{-6} T^2 - 726.891 \times 10^{-9} T^3 + 235.464 \times 10^{-12} T^4$$

 $T = 1000 \text{ to } 3000 \text{ K}$ 

$$C_p(T) = 127.074 + 11.895 \times 10^{-3} T - 61.686 \times 10^5 T^{-2} - 1.810 \times 10^{-6} T^2$$

$$-(G^\circ(T) - H^\circ(298))/T = 324.036 + 126.262 \times 10^{-3} T - 24.8214 \times 10^{-6} T^2 + 2.3812 \times 10^{-9} T^3$$

Table 13. Thermodynamic functions for NpO<sub>3</sub>(g). (p° = 1 bar)

T (K)	S°(T) (J/mol-K)	H°(T)-H°(298) (kJ/mol)	C <sub>p</sub> (T) (J/mol-K)	-(G°(T) - H°(298))/T (J/mol-K)
298.15	315.895	0.000	70.246	315.895
300	316.330	0.130	70.443	315.896
400	337.873	7.639	79.010	318.775
500	356.043	15.790	83.409	324.462
600	371.428	24.231	85.094	331.043
700	384.585	32.767	85.490	337.775
800	395.997	41.313	85.386	344.356
900	406.040	49.839	85.138	350.663
1000	414.997	58.341	84.893	356.656
1100	423.079	66.820	84.702	362.333
1200	430.443	75.283	84.581	367.707
1300	437.211	83.738	84.527	372.796
1400	443.475	92.191	84.536	377.624
1500	449.309	100.647	84.596	382.211
1600	454.772	109.112	84.699	386.577
1700	459.910	117.588	84.837	390.741
1800	464.764	126.080	85.001	394.720
1900	469.365	134.589	85.184	398.528
2000	473.739	143.117	85.380	402.180
2100	477.910	151.665	85.583	405.688
2200	481.896	160.234	85.788	409.062
2300	485.714	168.823	85.992	412.312
2400	489.378	177.432	86.192	415.448
2500	492.900	186.061	86.384	418.476
2600	496.292	194.709	86.568	421.404
2700	499.562	203.374	86.741	424.238
2800	502.720	212.057	86.903	426.985
2900	505.772	220.754	87.053	429.650
3000	508.726	229.467	87.191	432.237

T = 298 to 1000 K

$$C_p(T) = 93.414 - 2.928 \times 10^{-3} T - 19.591 \times 10^5 T^{-2} - 3.792 \times 10^{-6} T^2$$

$$-(G^\circ(T) - H^\circ(298))/T = 341.106 - 219.072 \times 10^{-3} T + 593.340 \times 10^{-6} T^2 - 529.885 \times 10^{-9} T^3 + 171.193 \times 10^{-12} T^4$$

T = 1000 to 3000 K

$$C_p(T) = 77.185 + 4.497 \times 10^{-3} T + 36.941 \times 10^5 T^{-2} - 0.428 \times 10^{-6} T^2$$

$$-(G^\circ(T) - H^\circ(298))/T = 283.195 + 91.709 \times 10^{-3} T - 20.2950 \times 10^{-6} T^2 + 2.0999 \times 10^{-9} T^3$$

Table 14. Thermodynamic functions for  $\text{NpO}_2\text{Cl}_2(\text{g})$ . ( $p^\circ = 1 \text{ bar}$ )

T (K)	$S^\circ(T)$ (J/mol-K)	$H^\circ(T) - H^\circ(298)$ (kJ/mol)	$C_p(T)$ (J/mol-K)	$-(G^\circ(T) - H^\circ(298))/T$ (J/mol-K)
298.15	359.630	0.000	94.460	359.630
300	360.215	0.175	94.683	359.631
400	388.849	10.151	103.934	363.472
500	412.601	20.803	108.478	370.994
600	432.558	31.752	110.181	379.638
700	449.582	42.796	110.564	388.445
800	464.341	53.849	110.443	397.030
900	477.334	64.880	110.179	405.245
1000	488.929	75.885	109.919	413.044
1100	499.395	86.866	109.717	420.426
1200	508.936	97.831	109.585	427.410
1300	517.705	108.785	109.524	434.023
1400	525.821	119.737	109.526	440.294
1500	533.379	130.692	109.581	446.251
1600	540.454	141.655	109.680	451.920
1700	547.107	152.629	109.813	457.325
1800	553.388	163.619	109.974	462.489
1900	559.339	174.625	110.154	467.431
2000	564.994	185.650	110.348	472.169
2100	570.383	196.695	110.548	476.719
2200	575.530	207.760	110.752	481.094
2300	580.458	218.845	110.954	485.308
2400	585.184	229.950	111.152	489.372
2500	589.726	241.075	111.343	493.296
2600	594.096	252.219	111.526	497.089
2700	598.309	263.380	111.698	500.760
2800	602.374	274.558	111.859	504.317
2900	606.302	285.751	112.009	507.767
3000	610.101	296.959	112.146	511.115

 $T = 298 \text{ to } 1000 \text{ K}$ 

$$C_p(T) = 121.114 - 7.731 \times 10^{-3} T - 21.597 \times 10^5 T^{-2} - 1.451 \times 10^{-6} T^2$$

$$-(G^\circ(T) - H^\circ(298))/T = 392.576 - 287.867 \times 10^{-3} T + 783.423 \times 10^{-6} T^2 - 703.074 \times 10^{-9} T^3 + 288.021 \times 10^{-12} T^4$$

 $T = 1000 \text{ to } 3000 \text{ K}$ 

$$C_p(T) = 102.172 + 4.471 \times 10^{-3} T + 37.548 \times 10^5 T^{-2} - 0.424 \times 10^{-6} T^2$$

$$-(G^\circ(T) - H^\circ(298))/T = 317.891 + 118.598 \times 10^{-3} T - 26.0194 \times 10^{-6} T^2 + 2.6547 \times 10^{-9} T^3$$

Table 15. Thermodynamic functions for  $\text{NpO}_2\text{F}_2(\text{g})$ . ( $p^\circ = 1 \text{ bar}$ )

T (K)	$S^\circ(T)$ (J/mol-K)	$H^\circ(T)-H^\circ(298)$ (kJ/mol)	$C_p(T)$ (J/mol-K)	$-(G^\circ(T)-H^\circ(298))/T$ (J/mol-K)
298.15	334.284	0.000	88.825	334.284
300	334.834	0.165	89.091	334.286
400	362.138	9.682	100.210	337.932
500	385.191	20.024	105.889	345.143
600	404.744	30.752	108.298	353.491
700	421.514	41.632	109.141	362.040
800	436.104	52.559	109.333	370.406
900	448.981	63.491	109.290	378.435
1000	460.491	74.415	109.193	386.075
1100	470.894	85.330	109.112	393.321
1200	480.386	96.239	109.075	400.187
1300	489.117	107.147	109.087	406.696
1400	497.203	118.058	109.148	412.875
1500	504.737	128.978	109.251	418.751
1600	511.792	139.910	109.389	424.348
1700	518.428	150.857	109.556	429.689
1800	524.695	161.821	109.744	434.795
1900	530.634	172.806	109.947	439.684
2000	536.279	183.811	110.161	444.374
2100	541.659	194.838	110.378	448.879
2200	546.799	205.887	110.597	453.214
2300	551.720	216.957	110.812	457.391
2400	556.441	228.049	111.022	461.420
2500	560.977	239.161	111.223	465.312
2600	565.343	250.293	111.415	469.076
2700	569.551	261.444	111.595	472.720
2800	573.613	272.612	111.763	476.251
2900	577.537	283.796	111.919	479.677
3000	581.334	294.995	112.062	483.002

T = 298 to 1000 K

$$C_p(T) = 116.873 - 0.320 \times 10^{-3} T - 24.522 \times 10^5 T^{-2} - 5.075 \times 10^{-6} T^2$$

$$-(G^\circ(T)-H^\circ(298))/T = 366.239 - 277.572 \times 10^{-3} T + 751.502 \times 10^{-6} T^2 - 670.803 \times 10^{-9} T^3 + 216.742 \times 10^{-12} T^4$$

T = 1000 to 3000 K

$$C_p(T) = 102.102 + 4.514 \times 10^{-3} T + 30.629 \times 10^5 T^{-2} - 0.431 \times 10^{-6} T^2$$

$$-(G^\circ(T)-H^\circ(298))/T = 292.956 + 115.714 \times 10^{-3} T - 25.0585 \times 10^{-6} T^2 + 2.5370 \times 10^{-9} T^3$$

Table 16. Thermodynamic functions for  $\text{NpO}_2(\text{OH})_2(g)$ . ( $p^\circ = 1 \text{ bar}$ )

T (K)	$S^\circ(T)$ (J/mol-K)	$H^\circ(T)-H^\circ(298)$ (kJ/mol)	$C_p(T)$ (J/mol-K)	$-(G^\circ(T)-H^\circ(298))/T$ (J/mol-K)
298.15	377.244	0.000	106.587	377.244
300	377.904	0.197	106.867	377.246
400	410.468	11.546	119.157	381.602
500	437.895	23.851	126.193	390.194
600	461.264	36.673	129.869	400.141
700	481.451	49.772	131.931	410.348
800	499.164	63.038	133.343	420.366
900	514.939	76.433	134.527	430.014
1000	529.171	89.942	135.642	439.229
1100	542.150	103.561	136.735	448.004
1200	554.094	117.288	137.812	456.354
1300	565.167	131.122	138.864	464.303
1400	575.495	145.060	139.885	471.881
1500	585.180	159.098	140.866	479.115
1600	594.301	173.232	141.804	486.032
1700	602.925	187.457	142.695	492.656
1800	611.105	201.769	143.539	499.012
1900	618.888	216.163	144.335	505.118
2000	626.310	230.634	145.083	510.993
2100	633.406	245.178	145.785	516.655
2200	640.203	259.790	146.442	522.117
2300	646.727	274.465	147.054	527.394
2400	652.997	289.199	147.623	532.498
2500	659.035	303.988	148.152	537.439
2600	664.855	318.828	148.642	542.229
2700	670.473	333.716	149.094	546.875
2800	675.903	348.646	149.511	551.387
2900	681.156	363.617	149.894	555.771
3000	686.244	378.624	150.246	560.036

T = 298 to 1000 K

$$C_p(T) = 130.048 + 14.356 \times 10^{-3} T - 24.228 \times 10^5 T^{-2} - 6.521 \times 10^{-6} T^2$$

$$-(G^\circ(T)-H^\circ(298))/T = 414.908 - 327.746 \times 10^{-3} T + 888.046 \times 10^{-6} T^2 - 791.981 \times 10^{-9} T^3 + 256.042 \times 10^{-12} T^4$$

T = 1000 to 3000 K

$$C_p(T) = 121.533 + 16.145 \times 10^{-3} T + 1.348 \times 10^5 T^{-2} - 2.197 \times 10^{-6} T^2$$

$$-(G^\circ(T)-H^\circ(298))/T = 328.185 + 136.344 \times 10^{-3} T - 27.9953 \times 10^{-6} T^2 + 2.7721 \times 10^{-9} T^3$$

Table 17. Thermodynamic functions for PuO<sub>3</sub>(g). (p° = 1 bar)

T (K)	S°(T) (J/mol-K)	H°(T)-H°(298) (kJ/mol)	C <sub>p</sub> (T) (J/mol-K)	-(G°(T)-H°(298))/T (J/mol-K)
298.15	316.102	0.000	69.153	316.102
300	316.531	0.128	69.311	316.104
400	337.505	7.436	76.355	318.915
500	355.061	15.311	80.787	324.438
600	370.041	23.532	83.382	330.821
700	383.015	31.950	84.838	337.372
800	394.401	40.478	85.634	343.804
900	404.515	49.065	86.070	349.998
1000	413.597	57.686	86.321	355.911
1100	421.833	66.327	86.487	361.536
1200	429.364	74.982	86.625	366.879
1300	436.303	83.652	86.765	371.956
1400	442.739	92.336	86.922	376.785
1500	448.742	101.037	87.102	381.384
1600	454.370	109.757	87.309	385.771
1700	459.670	118.499	87.541	389.964
1800	464.680	127.266	87.799	393.977
1900	469.435	136.060	88.079	397.824
2000	473.960	144.883	88.379	401.519
2100	478.280	153.736	88.698	405.072
2200	482.414	162.623	89.031	408.494
2300	486.379	171.543	89.378	411.795
2400	490.190	180.499	89.734	414.983
2500	493.861	189.490	90.097	418.065
2600	497.402	198.518	90.466	421.049
2700	500.823	207.583	90.836	423.940
2800	504.133	216.685	91.206	426.745
2900	507.340	225.824	91.573	429.470
3000	510.451	235.000	91.935	432.117

T = 298 to 1000 K

$$C_p(T) = 73.745 + 31.894 \times 10^{-3} T - 11.135 \times 10^5 T^{-2} - 1.835 \times 10^{-6} T^2$$

$$-(G^\circ(T)-H^\circ(298))/T = 340.056 - 208.933 \times 10^{-3} T + 566.892 \times 10^{-6} T^2 - 505.402 \times 10^{-9} T^3 + 163.324 \times 10^{-12} T^4$$

T = 1000 to 3000 K

$$C_p(T) = 84.074 + 0.971 \times 10^{-3} T + 7.872 \times 10^5 T^{-2} + 0.547 \times 10^{-6} T^2$$

$$-(G^\circ(T)-H^\circ(298))/T = 283.967 + 88.978 \times 10^{-3} T - 18.8792 \times 10^{-6} T^2 + 1.8954 \times 10^{-9} T^3$$

Table 18. Thermodynamic functions for PuO<sub>2</sub>Cl<sub>2</sub>(g). (p° = 1 bar)

T (K)	S°(T) (J/mol-K)	H°(T)-H°(298) (kJ/mol)	C <sub>p</sub> (T) (J/mol-K)	-(G°(T)-H°(298))/T (J/mol-K)
298.15	359.858	0.000	93.368	359.858
300	360.436	0.173	93.551	359.860
400	388.502	9.947	101.280	363.634
500	411.639	20.324	105.856	370.990
600	431.193	31.053	108.469	379.437
700	448.033	41.980	109.913	388.062
800	462.766	53.014	110.691	396.499
900	475.830	64.106	111.110	404.601
1000	487.550	75.230	111.347	412.320
1100	498.170	86.373	111.502	419.650
1200	507.878	97.529	111.630	426.603
1300	516.818	108.699	111.762	433.204
1400	525.106	119.882	111.912	439.476
1500	532.833	131.082	112.087	445.445
1600	540.073	142.301	112.289	451.135
1700	546.887	153.541	112.518	456.569
1800	553.326	164.805	112.772	461.767
1900	559.430	176.096	113.049	466.748
2000	565.236	187.415	113.347	471.529
2100	570.774	198.766	113.663	476.124
2200	576.069	210.149	113.995	480.547
2300	581.144	221.565	114.340	484.812
2400	586.018	233.017	114.694	488.928
2500	590.707	244.504	115.057	492.906
2600	595.227	256.028	115.424	496.755
2700	599.590	267.589	115.793	500.483
2800	603.808	279.187	116.162	504.098
2900	607.891	290.821	116.528	507.607
3000	611.847	302.492	116.889	511.016

T = 298 to 1000 K

$$C_p(T) = 101.452 + 27.087 \times 10^{-3} T - 13.142 \times 10^5 T^{-2} - 16.002 \times 10^{-6} T^2$$

$$-(G^\circ(T)-H^\circ(298))/T = 391.526 - 277.564 \times 10^{-3} T + 756.542 \times 10^{-6} T^2 - 678.121 \times 10^{-9} T^3 + 219.972 \times 10^{-12} T^4$$

T = 1000 to 3000 K

$$C_p(T) = 109.057 + 0.948 \times 10^{-3} T + 8.497 \times 10^5 T^{-2} + 0.550 \times 10^{-6} T^2$$

$$-(G^\circ(T)-H^\circ(298))/T = 318.361 + 116.470 \times 10^{-3} T - 24.9576 \times 10^{-6} T^2 + 2.5159 \times 10^{-9} T^3$$

Table 19. Thermodynamic functions for PuO<sub>2</sub>F<sub>2</sub>(g). (p° = 1 bar)

T (K)	S°(T) (J/mol-K)	H°(T)-H°(298) (kJ/mol)	C <sub>p</sub> (T) (J/mol-K)	-(G°(T)-H°(298))/T (J/mol-K)
298.15	334.496	0.000	87.732	334.496
300	335.040	0.163	87.959	334.498
400	361.774	9.478	97.556	338.078
500	384.213	19.545	103.267	345.123
600	403.362	30.053	106.587	353.274
700	419.949	40.815	108.490	361.641
800	434.513	51.724	109.581	369.859
900	447.460	62.717	110.222	377.775
1000	459.096	73.760	110.621	385.335
1100	469.653	84.837	110.897	392.528
1200	479.312	95.938	111.119	399.363
1300	488.214	107.060	111.325	405.860
1400	496.472	118.203	111.534	412.041
1500	504.174	129.368	111.757	417.929
1600	511.394	140.555	111.998	423.548
1700	518.192	151.768	112.260	428.917
1800	524.617	163.008	112.541	434.057
1900	530.709	174.277	112.842	438.985
2000	536.505	185.577	113.160	443.717
2100	542.034	196.909	113.493	448.268
2200	547.322	208.276	113.840	452.651
2300	552.390	219.678	114.198	456.878
2400	557.258	231.116	114.564	460.960
2500	561.943	242.591	114.936	464.906
2600	566.458	254.103	115.312	468.726
2700	570.817	265.653	115.690	472.427
2800	575.031	277.241	116.066	476.016
2900	579.110	288.866	116.439	479.501
3000	583.064	300.528	116.806	482.888

T = 298 to 1000 K

$$C_p(T) = 97.212 + 34.500 \times 10^{-3} T - 16.068 \times 10^5 T^{-2} - 19.628 \times 10^{-6} T^2$$

$$-(G^\circ(T)-H^\circ(298))/T = 365.158 - 267.181 \times 10^{-3} T + 724.423 \times 10^{-6} T^2 - 645.660 \times 10^{-9} T^3 + 208.627 \times 10^{-12} T^4$$

T = 1000 to 3000 K

$$C_p(T) = 108.992 + 0.986 \times 10^{-3} T + 1.561 \times 10^5 T^{-2} + 0.544 \times 10^{-6} T^2$$

$$-(G^\circ(T)-H^\circ(298))/T = 293.403 + 113.598 \times 10^{-3} T - 24.0031 \times 10^{-6} T^2 + 2.3992 \times 10^{-9} T^3$$

Table 20. Thermodynamic functions for PuO<sub>2</sub>(OH)<sub>2</sub>(g). (p° = 1 bar)

T (K)	S°(T) (J/mol-K)	H°(T)-H°(298) (kJ/mol)	C <sub>p</sub> (T) (J/mol-K)	-(G°(T)-H°(298))/T (J/mol-K)
298.15	377.460	0.000	105.494	377.460
300	378.114	0.195	105.734	377.462
400	410.108	11.343	116.503	381.751
500	436.921	23.372	123.572	390.177
600	459.885	35.974	128.157	399.928
700	479.889	48.955	131.279	409.953
800	497.577	62.204	133.591	419.822
900	513.422	75.659	135.458	429.357
1000	527.779	89.287	137.070	438.493
1100	540.913	103.067	138.520	447.215
1200	553.023	116.987	139.856	455.534
1300	564.268	131.036	141.102	463.471
1400	574.768	145.205	142.271	471.050
1500	584.621	159.487	143.372	478.296
1600	593.908	173.877	144.413	485.235
1700	602.693	188.368	145.399	491.888
1800	611.030	202.955	146.336	498.277
1900	618.966	217.634	147.229	504.422
2000	626.540	232.400	148.083	510.340
2100	633.785	247.249	148.900	516.047
2200	640.730	262.179	149.685	521.558
2300	647.400	277.185	150.439	526.885
2400	653.819	292.266	151.166	532.041
2500	660.004	307.418	151.865	537.037
2600	665.973	322.638	152.539	541.882
2700	671.742	337.925	153.188	546.585
2800	677.325	353.275	153.813	551.155
2900	682.733	368.686	154.413	555.600
3000	687.977	384.157	154.989	559.925

T = 298 to 1000 K

$$C_p(T) = 110.400 + 49.143 \times 10^{-3} T - 15.780 \times 10^5 T^{-2} - 21.055 \times 10^{-6} T^2$$

$$-(G^\circ(T)-H^\circ(298))/T = 413.869 - 317.640 \times 10^{-3} T + 861.699 \times 10^{-6} T^2 - 767.626 \times 10^{-9} T^3 + 248.229 \times 10^{-12} T^4$$

T = 1000 to 3000 K

$$C_p(T) = 128.411 + 12.627 \times 10^{-3} T - 27.675 \times 10^5 T^{-2} - 1.224 \times 10^{-6} T^2$$

$$-(G^\circ(T)-H^\circ(298))/T = 328.643 + 134.217 \times 10^{-3} T - 26.9344 \times 10^{-6} T^2 + 2.6335 \times 10^{-9} T^3$$

Table 21. Thermodynamic functions for AmO<sub>3</sub>(g). (p° = 1 bar)

T (K)	S°(T) (J/mol-K)	H°(T)-H°(298) (kJ/mol)	C <sub>p</sub> (T) (J/mol-K)	-(G°(T)-H°(298))/T (J/mol-K)
298.15	317.708	0.000	71.538	317.708
300	318.151	0.132	71.693	317.709
400	339.738	7.652	78.057	320.609
500	357.550	15.640	81.308	326.270
600	372.525	23.856	82.809	332.765
700	385.346	32.174	83.455	339.383
800	396.509	40.534	83.704	345.841
900	406.373	48.909	83.775	352.030
1000	415.200	57.286	83.772	357.913
1100	423.183	65.662	83.746	363.490
1200	430.469	74.036	83.723	368.772
1300	437.170	82.408	83.719	373.779
1400	443.375	90.781	83.743	378.531
1500	449.154	99.157	83.800	383.049
1600	454.565	107.542	83.894	387.352
1700	459.655	115.937	84.028	391.457
1800	464.463	124.349	84.202	395.380
1900	469.021	132.779	84.416	399.137
2000	473.357	141.233	84.670	402.740
2100	477.495	149.715	84.963	406.202
2200	481.455	158.227	85.291	409.534
2300	485.254	166.774	85.653	412.744
2400	488.908	175.359	86.046	415.842
2500	492.429	183.984	86.468	418.835
2600	495.829	192.653	86.914	421.731
2700	499.118	201.368	87.382	424.537
2800	502.304	210.130	87.869	427.258
2900	505.396	218.942	88.370	429.899
3000	508.401	227.804	88.882	432.466

T = 298 to 1000 K

$$C_p(T) = 86.059 + 3.057 \times 10^{-3}T - 13.430 \times 10^5 T^{-2} - 4.077 \times 10^{-6}T^2$$

$$-(G^\circ(T)-H^\circ(298))/T = 342.274 - 215.134 \times 10^{-3}T + 586.366 \times 10^{-6}T^2 - 526.456 \times 10^{-9}T^3 + 170.890 \times 10^{-12}T^4$$

T = 1000 to 3000 K

$$C_p(T) = 85.499 - 3.602 \times 10^{-3}T + 3.392 \times 10^5 T^{-2} + 1.579 \times 10^{-6}T^2$$

$$-(G^\circ(T)-H^\circ(298))/T = 286.114 + 89.344 \times 10^{-3}T - 19.4763 \times 10^{-6}T^2 + 1.9874 \times 10^{-9}T^3$$

Table 22. Thermodynamic functions for AmO<sub>2</sub>Cl<sub>2</sub>(g). (p° = 1 bar)

T (K)	S°(T) (J/mol-K)	H°(T)-H°(298) (kJ/mol)	C <sub>p</sub> (T) (J/mol-K)	-(G°(T)-H°(298))/T (J/mol-K)
298.15	361.488	0.000	95.753	361.488
300	362.081	0.177	95.933	361.490
400	390.760	10.163	102.981	365.352
500	414.153	20.653	106.377	372.847
600	433.701	31.377	107.896	381.406
700	450.388	42.203	108.530	390.098
800	464.899	53.070	108.761	398.561
900	477.713	63.950	108.816	406.658
1000	489.177	74.831	108.799	414.347
1100	499.545	85.709	108.761	421.628
1200	509.007	96.583	108.728	428.521
1300	517.709	107.455	108.716	435.052
1400	525.766	118.327	108.733	441.247
1500	533.270	129.203	108.784	447.135
1600	540.293	140.085	108.874	452.740
1700	546.897	150.979	109.004	458.086
1800	553.133	161.887	109.175	463.195
1900	559.041	172.815	109.386	468.085
2000	564.658	183.766	109.638	472.775
2100	570.014	194.744	109.928	477.279
2200	575.135	205.753	110.254	481.611
2300	580.044	216.796	110.615	485.785
2400	584.760	227.877	111.007	489.811
2500	589.300	238.998	111.427	493.701
2600	593.679	250.163	111.872	497.462
2700	597.909	261.373	112.339	501.105
2800	602.004	272.631	112.825	504.635
2900	605.972	283.939	113.325	508.062
3000	609.822	295.297	113.836	511.390

T = 298 to 1000 K

$$C_p(T) = 113.757 - 1.743 \times 10^{-3} T - 15.436 \times 10^5 T^{-2} - 1.736 \times 10^{-6} T^2$$

$$-(G^\circ(T)-H^\circ(298))/T = 393.787 - 283.894 \times 10^{-3} T + 776.337 \times 10^{-6} T^2 - 699.507 \times 10^{-9} T^3 + 227.661 \times 10^{-12} T^4$$

T = 1000 to 3000 K

$$C_p(T) = 110.471 - 3.618 \times 10^{-3} T + 4.077 \times 10^5 T^{-2} + 1.582 \times 10^{-6} T^2$$

$$-(G^\circ(T)-H^\circ(298))/T = 320.532 + 116.839 \times 10^{-3} T - 25.5572 \times 10^{-6} T^2 + 2.6083 \times 10^{-9} T^3$$

Table 23. Thermodynamic functions for AmO<sub>2</sub>F<sub>2</sub>(g). (p° = 1 bar)

T (K)	S°(T) (J/mol-K)	H°(T)-H°(298) (kJ/mol)	C <sub>p</sub> (T) (J/mol-K)	-(G°(T)-H°(298))/T (J/mol-K)
298.15	336.108	0.000	90.118	336.108
300	336.666	0.167	90.341	336.110
400	364.014	9.695	99.258	339.778
500	386.708	19.873	103.788	346.962
600	405.852	30.376	106.014	355.224
700	422.286	41.039	107.107	363.659
800	436.628	51.780	107.651	371.903
900	449.325	62.560	107.927	379.813
1000	460.704	73.361	108.072	387.343
1100	471.009	84.173	108.156	394.488
1200	480.423	94.991	108.218	401.263
1300	489.087	105.816	108.279	407.690
1400	497.114	116.648	108.355	413.794
1500	504.593	127.488	108.454	419.601
1600	511.596	138.340	108.583	425.134
1700	518.184	149.206	108.746	430.416
1800	524.405	160.090	108.944	435.466
1900	530.301	170.996	109.179	440.304
2000	535.908	181.927	109.451	444.945
2100	541.256	192.887	109.758	449.405
2200	546.370	203.880	110.100	453.697
2300	551.272	214.908	110.473	457.833
2400	555.982	225.976	110.876	461.825
2500	560.517	237.084	111.307	465.683
2600	564.891	248.238	111.761	469.415
2700	569.118	259.437	112.236	473.030
2800	573.208	270.685	112.729	476.535
2900	577.173	281.984	113.235	479.937
3000	581.021	293.333	113.752	483.243

T = 298 to 1000 K

$$C_p(T) = 109.519 + 5.667 \times 10^{-3} T - 18.362 \times 10^5 T^{-2} - 5.362 \times 10^{-6} T^2$$

$$-(G^\circ(T)-H^\circ(298))/T = 367.400 - 273.497 \times 10^{-3} T + 744.172 \times 10^{-6} T^2 - 666.985 \times 10^{-9} T^3 + 216.288 \times 10^{-12} T^4$$

T = 1000 to 3000 K

$$C_p(T) = 110.406 - 3.580 \times 10^{-3} T - 2.871 \times 10^5 T^{-2} + 1.575 \times 10^{-6} T^2$$

$$-(G^\circ(T)-H^\circ(298))/T = 295.559 + 113.959 \times 10^{-3} T - 24.5978 \times 10^{-6} T^2 + 2.4907 \times 10^{-9} T^3$$

Table 24. Thermodynamic functions for  $\text{AmO}_2(\text{OH})_2(\text{g})$ . ( $p^\circ = 1 \text{ bar}$ )

T (K)	$S^\circ(T)$ (J/mol-K)	$H^\circ(T)-H^\circ(298)$ (kJ/mol)	$C_p(T)$ (J/mol-K)	$-(G^\circ(T)-H^\circ(298))/T$ (J/mol-K)
298.15	379.076	0.000	107.880	379.076
300	379.744	0.200	108.117	379.078
400	412.352	11.559	118.204	383.455
500	439.421	23.700	124.092	392.020
600	462.380	36.298	127.584	401.883
700	482.231	49.179	129.897	411.975
800	499.695	62.259	131.661	421.871
900	515.291	75.502	133.163	431.400
1000	529.392	88.887	134.521	440.505
1100	542.273	102.403	135.779	449.180
1200	554.139	116.040	136.954	457.438
1300	565.145	129.792	138.056	465.305
1400	575.414	143.649	139.092	472.807
1500	585.044	157.608	140.070	479.972
1600	594.114	171.662	140.998	486.825
1700	602.689	185.806	141.886	493.391
1800	610.823	200.038	142.740	499.691
1900	618.563	214.353	143.567	505.745
2000	625.947	228.750	144.374	511.572
2100	633.011	243.227	145.165	517.188
2200	639.782	257.783	145.944	522.608
2300	646.286	272.416	146.715	527.844
2400	652.547	287.126	147.478	532.911
2500	658.582	301.911	148.236	537.818
2600	664.411	316.773	148.988	542.575
2700	670.048	331.709	149.735	547.193
2800	675.507	346.720	150.476	551.678
2900	680.800	361.804	151.210	556.040
3000	685.938	376.961	151.936	560.285

T = 298 to 1000 K

$$C_p(T) = 122.688 + 20.353 \times 10^{-3} T - 18.066 \times 10^5 T^{-2} - 6.814 \times 10^{-6} T^2$$

$$-(G^\circ(T)-H^\circ(298))/T = 416.110 - 323.915 \times 10^{-3} T + 881.329 \times 10^{-6} T^2 - 788.801 \times 10^{-9} T^3 + 255.824 \times 10^{-12} T^4$$

T = 1000 to 3000 K

$$C_p(T) = 129.835 + 8.054 \times 10^{-3} T - 32.156 \times 10^5 T^{-2} - 0.192 \times 10^{-6} T^2$$

$$-(G^\circ(T)-H^\circ(298))/T = 330.800 + 134.584 \times 10^{-3} T - 27.5321 \times 10^{-6} T^2 + 2.7255 \times 10^{-9} T^3$$

Table 25. Comparison of entropies previously calculated for  $\text{UO}_3(\text{g})$ ,  $\text{UO}_2\text{Cl}_2(\text{g})$ , and  $\text{UO}_2\text{F}_2(\text{g})$  with entropies calculated herein. ( $p^\circ = 1 \text{ bar}$ )

species	$S^\circ(298)$	previous			present study	
		$S^\circ(1000)$	$S^\circ(3000)$	$S^\circ(298)$	$S^\circ(1000)$	$S^\circ(3000)$
$\text{UO}_3(\text{g})$	309.7 <sup>a</sup>	400.7 <sup>a</sup>	497.5 <sup>a</sup>	308.7	398.3	488.4
$\text{UO}_2\text{Cl}_2(\text{g})$	377 <sup>b</sup>	---	---	352.4	472.2	589.7
$\text{UO}_2\text{F}_2(\text{g})$	348.9 <sup>c</sup>	466.7 <sup>c</sup>	---	327.0	443.8	560.9

<sup>a</sup>From reference [40]

<sup>b</sup>From reference [18]

<sup>c</sup>From reference [4]